

# Study the Critical Role of Admixtures in Cement Production: The Optimum State of Cassiterite ( $\text{SnO}_2$ ) Addition as a Natural Mineralizer-Oxide Influencing the Cement Properties

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## Abstract

In this work we evaluate the role of a natural mineralizer-oxide like cassiterite ( $\text{SnO}_2$ ) on the cement properties. In particular, we study the effect of different quantities of  $\text{SnO}_2$  with 0.5, 1.0, 1.5 and 2.0 wt% on burnability of industrial raw mix by free lime evaluation. We obtain four datasets, with successive increase of temperature at 1250°C, 1350°C, 1400°C and 1450°C. We study the produced cassiterite-added clinker with X-ray diffraction (XRD), thermal analysis (DTA) and scanning electron microscopy (SEM). Though, we characterize the new phases formed and whether, adding excess  $\text{SnO}_2$  is promote forms of  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$  influencing the final quality of cement.

**Keywords:** Cement Properties, Cassiterite, Burnability, Hydration

## 1. Introduction

Cement has a wide range of uses like in pottery, construction and manufacturing; all of them need a high-potential of energy consumption. Because of that, scientists and manufacturers use admixtures to achieve a balance between energy and quality. Such admixtures play, indirectly, an important role in the green gases emissions; though the lower the energy consumption the lower the gas emissions like  $\text{CO}_2$  [1]. Only small amounts of admixtures (<2 wt%) could control the temperature at which produced high-quality clinker [2].

Recently [3] and [4], study the influence of synthetic NaF, KF,  $\text{SnO}_2$  and  $\text{TiO}_2$  and their mixtures implying that they decrease the temperature at which starts the dissociation of the calcium carbonate from the raw mix. However, the influence of fluorides on burnability of raw mix is more intense compared with that of oxides. Besides, according to [5] the presence of  $\text{SnO}_2$  ~1.0 wt% in the raw mix lowers more intensively the values of free lime. Thus preferring the  $\text{C}_3\text{S}$  (alite) formation with add-

ing both oxides, fluorides and their mixtures.

In this work we evaluate the role of a natural mineralizer-oxide like cassiterite ( $\text{SnO}_2$ ) [e.g. 6] on the cement properties. In particular, we study the effect of different quantities of  $\text{SnO}_2$  with 0.5, 1.0, 1.5 and 2.0 wt% on burnability of industrial raw mix by free lime evaluation. We obtain four datasets with successive increase of temperature at 1250°C, 1350°C, 1400°C and 1450°C. The produced cassiterite-added clinker is studied with X-ray diffraction (XRD), thermal analysis (DTA) and scanning electron microscopy (SEM). Though, we characterize the new phases formed and whether adds excess  $\text{SnO}_2$  is promote forms of  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$  influencing the final quality of cement.

## 2. Experimental Work-Analytical Methods

For the current study we use primary material for the cement production, gained from the Titan S.A. factory. It has the following chemical composition (in wt%)  $\text{CaCO}_3$ : 79.53,  $\text{SiO}_2$ : 14.52,  $\text{Al}_2\text{O}_3$ : 3.82,  $\text{Fe}_2\text{O}_3$ : 2.13. The grain

size was nearly 90  $\mu\text{m}$ .

Industrial cassiterites  $\text{SnO}_2$ , granted by a large multinational ceramics industry in Chalkis, used in similar particle size to the raw meal. We produce five samples of raw meal weighting 220 gr, by adding cassiterites with increasing ratio of 0.0, 0.5, 1.0, 1.5 and 2.0 wt%. Afterwards, homogenization in a ball mill occurs and format of the samples in pellets. We burn pellets in a high-temperature oven at four different temperatures 1200°C, 1350°C, 1400°C and 1450°C.

Clinker studied using the following methods: 1) Differential thermal analysis (DTA) with raw meal samples weighting 60 mg. In particular, we used the Thermogravimetric Analyzer TGA/SDTA 851e METTLER TOLEDO's at the Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens. The air gas was nitrogen with 50  $\text{cm}^3/\text{min}$  flow. The study begins at 25°C with a constant rate 20°C/min until the maximum temperature of 1500°C. 2) We apply the method of X-ray diffraction (XRD) for determination of free-lime in clinker. Irradiating the powdered samples took place in the range between 3 and 75 degrees. We use amplified electronic scales of four decimals, which weighed 0,5 gr of ground clinker. We used 50 ml ethylene glycol and HCl 0.1 N and 1 N accordingly. 3) Secondary electron microscopy (SEM) analyses of two clinker samples heated at 1400°C, one cassiterite-free and the other's content was 2 wt%. The analyses performed using a JEOL JSM 5600 SEM equipped with a LINK ISIS 3000 energy dispersive system at the Department of Geology, University of Athens. Analytical conditions were 20 KV acceleration voltage, 0,5 nA probe current with acquisition time 50 sec. Covering the granules of the two samples with gold to avoid concentrating electrons.

Afterwards thermal treatment at 1450°C applied to transform clinker to cement; therefore we used plaster in powder form and in a rate of 5% w/w. Then followed a synalesis in a grinder for 10 min. From the resulted cement, we prepare pastes to study the hydration rate.

Pastes with different mode of cassiterite took place in disk-shaped format and placed in water for 1, 2, 7 and 28 days. At the end of the two days, we remove samples with cassiterite content 0.0, 0.5, 1.0, 1.5 and 2.0 wt% from the water and soaked them in acetone solution to stop the hydration. The samples placed in an oven at 1200°C for one day and then pulverized in a grinder. The total weight loss from pastes is attributed to chemical bounded water liberated during dehydration at 100°C - 300°C and dehydroxylation of portlandite at 450°C - 550°C. The results are presented in detail in **table 1**. Later, the samples analyzed with XRD to discover whether they had formed all the necessary steps. Also we study

the calcination loss in the samples. We repeat the procedure at the end of seven and twenty eight days.

### 3. Results and Discussion

For the study of clinker we use industrial raw mix with cassiterite as admixture in different quantities 0.5, 1.0, 1.5 and 2.0 wt%. We study the burnability of raw mix with TG and DTA thermal methods. The samples heated up to 900°C hold two endothermal peaks at ~200 and ~850°C which are because of dissociation of clay minerals and calcite respectively. The thermal range between 900°C - 1200°C doesn't add important knowledge into the thermal behavior of the studied samples. However, we prove the first appear of belite ( $\text{C}_2\text{S}$ ) by developing an exothermic peak above 1200°C. The early formation of belite (at <1200°C) is concurrent with the maximum cassiterite content (2 wt%; **Figure 1(a)**). A significant point at  $\text{SnO}_2 = 1$  wt% is the presence of a broad endothermal peak, covered the belite one, assigned to melt formation (**Figures 1(a) and (b)**).

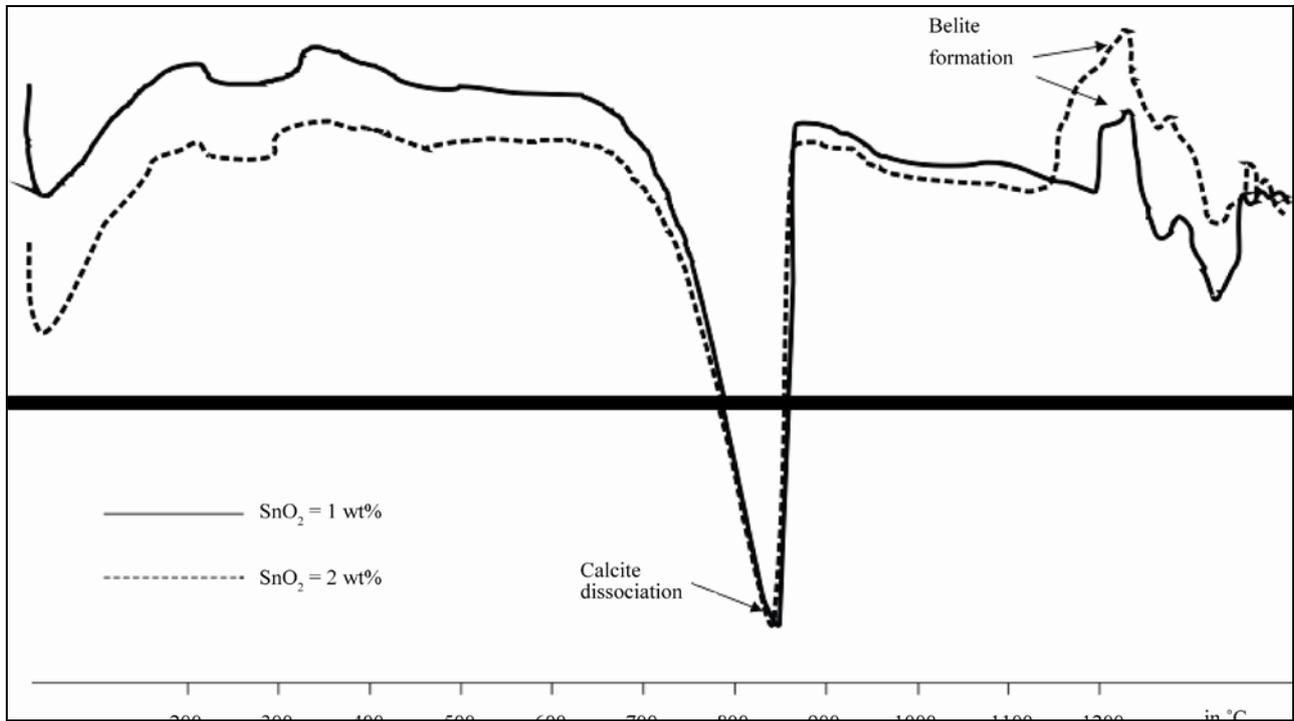
Evaluating X-ray diffraction diagrams before hydration (**Figures 2-4**) show the absence of calcite peak because of its completed dissociation at temperatures up to 1350°C. Since 1350°C formation of belite phases with minor amounts of  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ , CaO and  $\text{Ca}(\text{OH})_2$  components.  $\text{SiO}_2$  is absent. At 1400°C we obey all phases whereas alite ( $\text{C}_3\text{S}$ ) comes for first time; however decreasing of CaO content occurs. At higher temperatures (>1400°C) CaO is continuously decreasing; at  $\text{SnO}_2 = 1$  wt% CaO content drop down to its minimum value. Also we note the phase  $\text{Ca}_2\text{SnO}_4$  only in the sample heated at 1400 and 1450°C with cassiterite content at 2 wt%.

Evaluating X-ray diffraction diagrams after hydration (**Figures 5 and 6**) show that at 1 and 2 days a mixture of hydrated and non-hydrated phases occur. The main hydrated phase is  $\text{Ca}(\text{OH})_2$ . The samples of 7 and 28 days from hydration, showed a clear decrease of non-hydrated phases; the samples contain 1 wt% cassiterite point out the highest hydration rate (**Figures 7 and 8**).

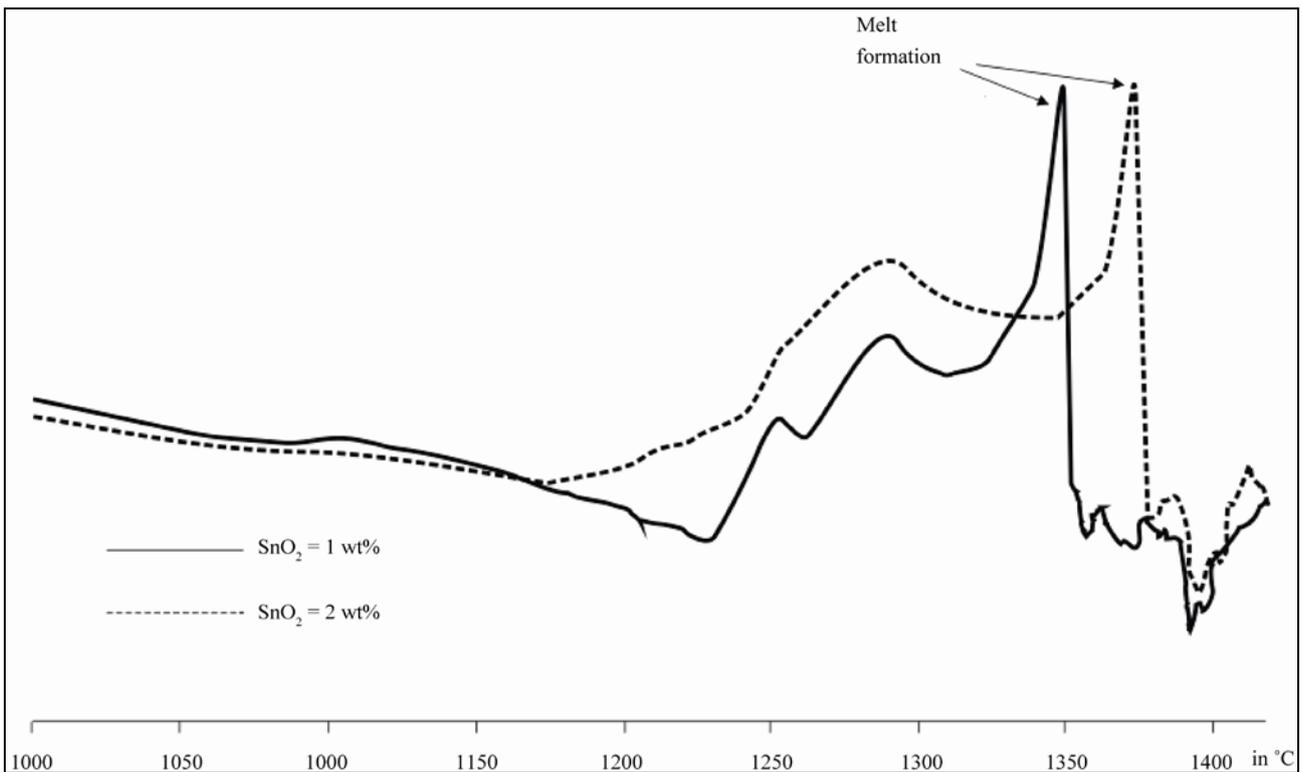
Determining fCaO and burnability rate suggest that cassiterite in the raw mix influences positively the heat treatment and lowers more intensively the values of free lime. We gain the best results at  $\text{SnO}_2 = 1$  wt% (**Figure 9**).

Calculating the water content bounded on pastes shows the cassiterite-free sample takes over the highest hydration rate at 1.2 and 7 days (**Table 1**). However at 28 days the highest hydration rate occupied in the sample with 1 wt% cassiterite (**Table 1**).

SEM investigation suggests the  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  phases have similar shape with or without adding cassiterite in the primary material. However the presence of cassiterite



(a)



(b)

**Figure 1. Comparison of DTA thermal analysis results of samples with SnO<sub>2</sub> = 1 and 2 wt% respectively. (a) At ~850°C an endothermic peak occurs due to calcite dissociation. At 1200°C developing an exothermic peak suggests the first presence of belite (C<sub>2</sub>S). The early formation of belite (at <1200°C) is concurrent with the maximum of cassiterite content (SnO<sub>2</sub> = 2 wt%). (b) Early melt formation at SnO<sub>2</sub> = 1 wt% probably hide forming belite.**

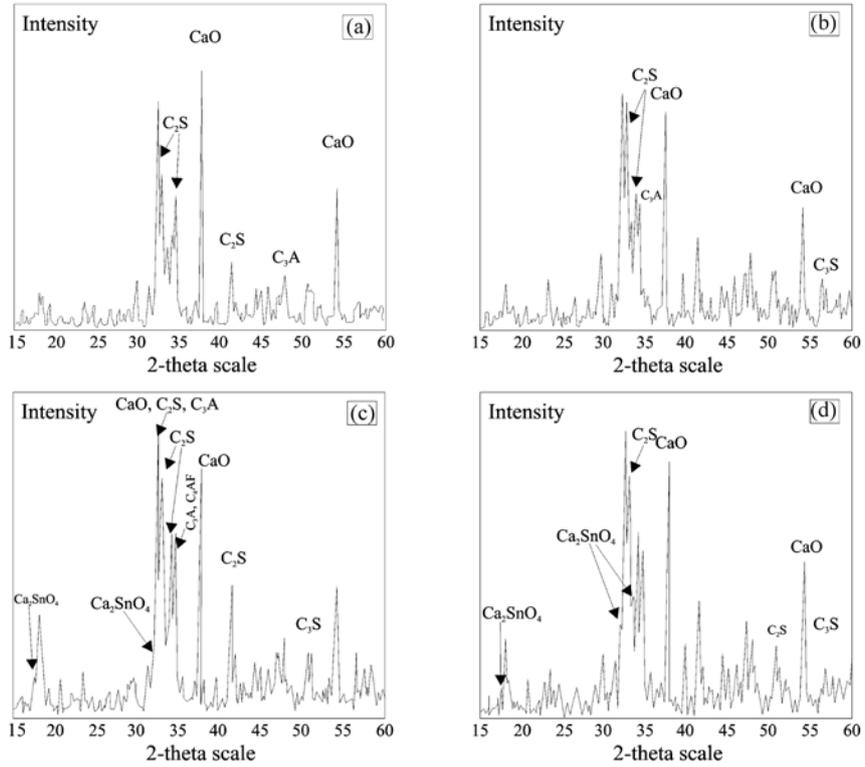


Figure 2. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the clinker at 1350C with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

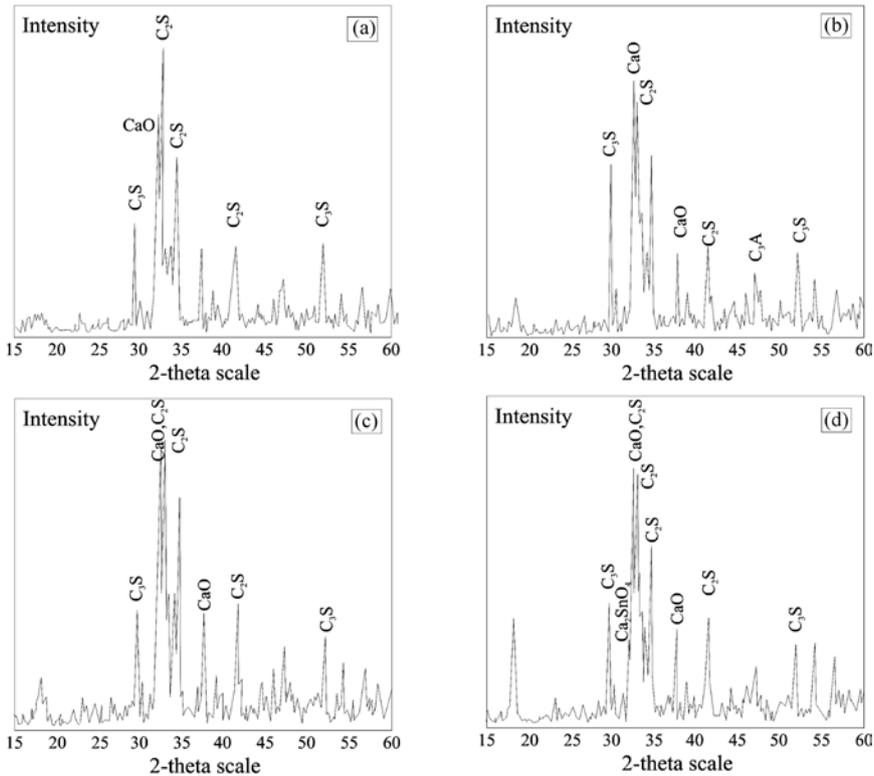


Figure 3. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the clinker at 1400C with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

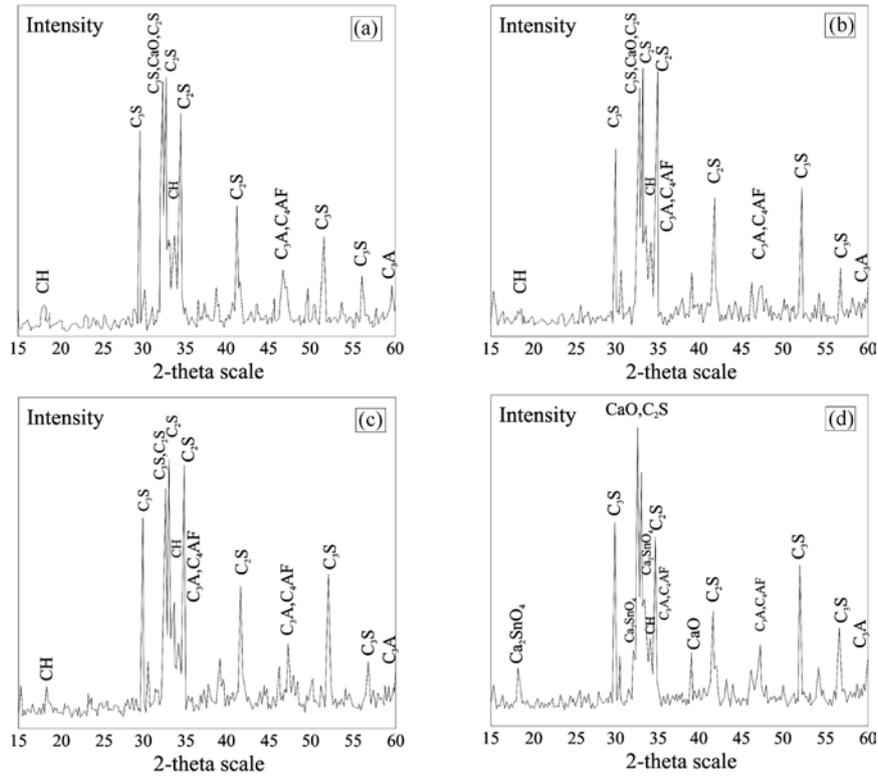


Figure 4. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the clinker at 1450°C with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

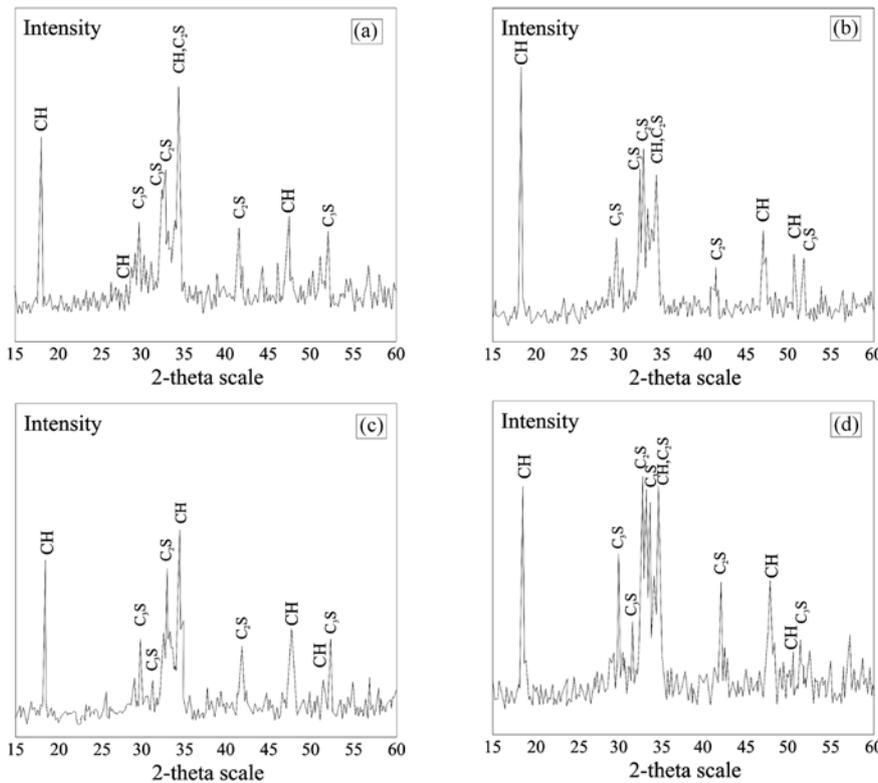


Figure 5. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the hydrated pastes at 1 day with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

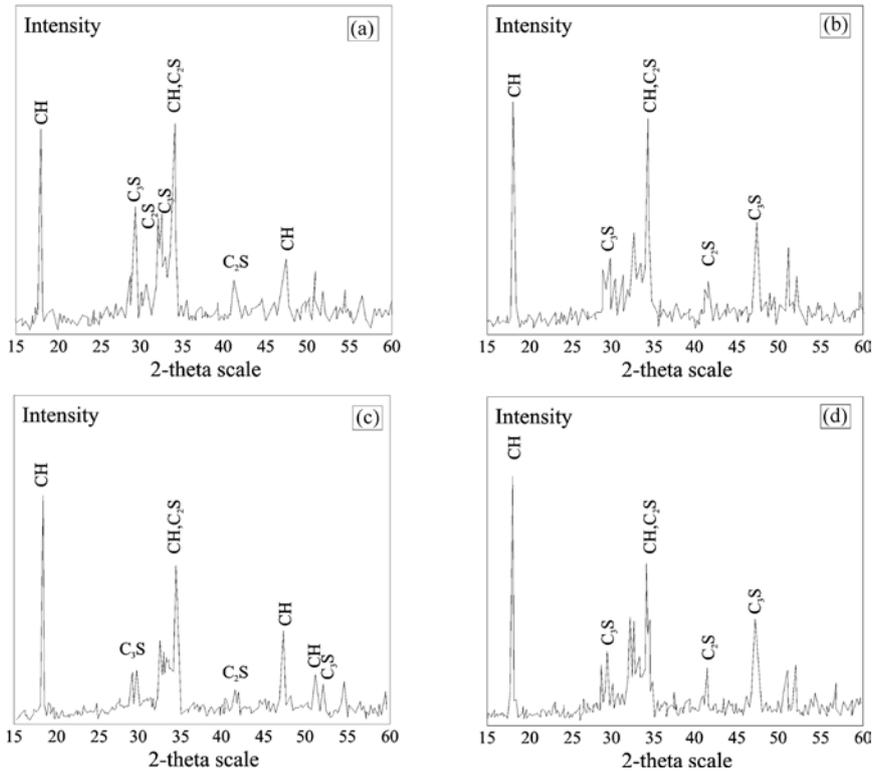


Figure 6. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the hydrated pastes at 2 days with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

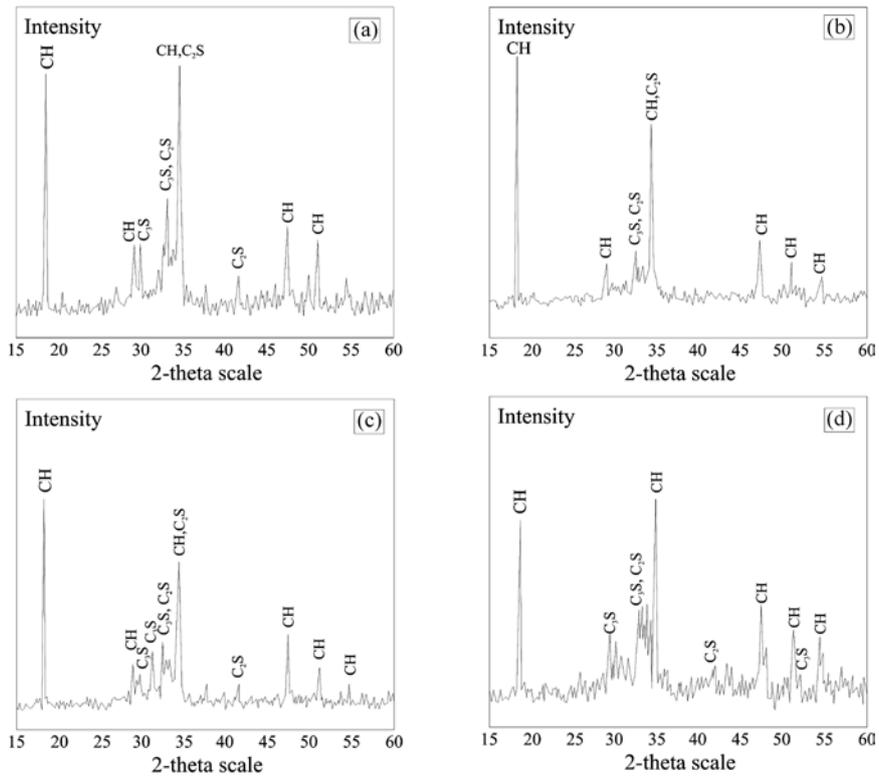


Figure 7. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the hydrated pastes at 7 days with SnO<sub>2</sub>. (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

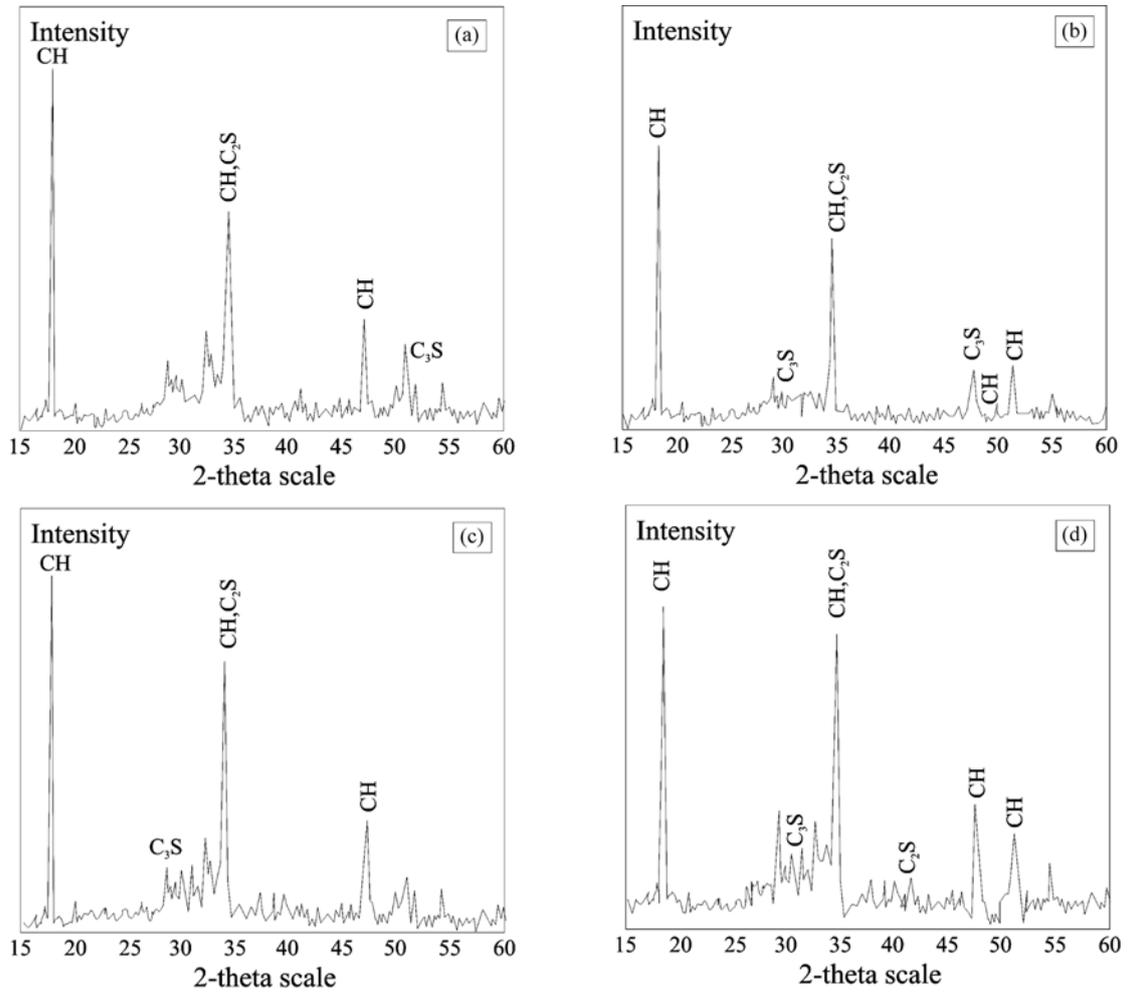


Figure 8. X-ray diffractograms for  $2\theta$  3 - 75 (CuK $\alpha$  radiation) showing the hydrated pastes at 28 days with SnO<sub>2</sub>, (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt%.

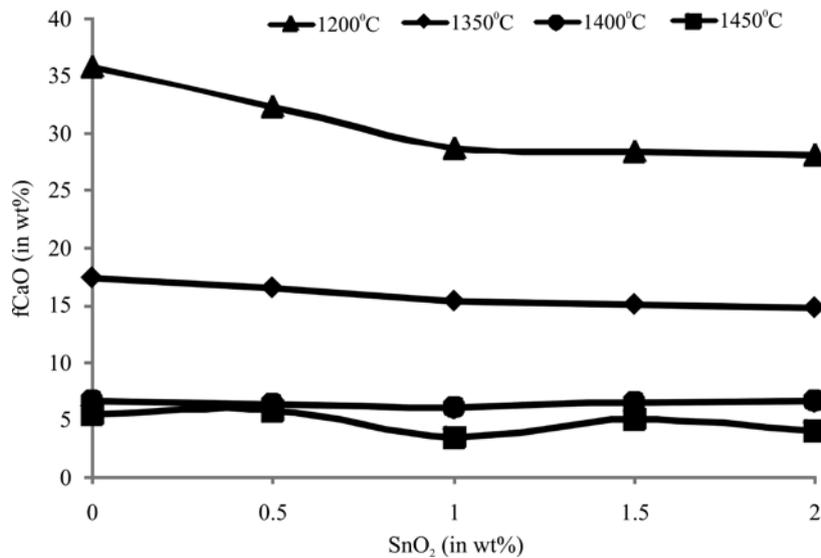


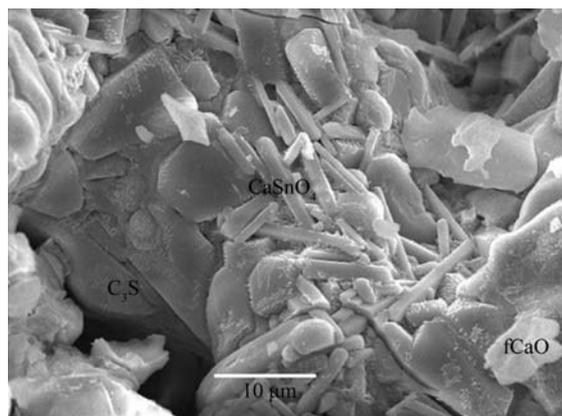
Figure 9. fCaO-SnO<sub>2</sub> diagram showing the ideal fCaO conditions at various temperatures. We remark that at SnO<sub>2</sub> = 1 wt% the fCaO become minimum, influencing the burnability behavior.

**Table 1. Experimental data showing the calculated water bounded on pastes with different cassiterite content at 1, 2, 7 and 28 days.**

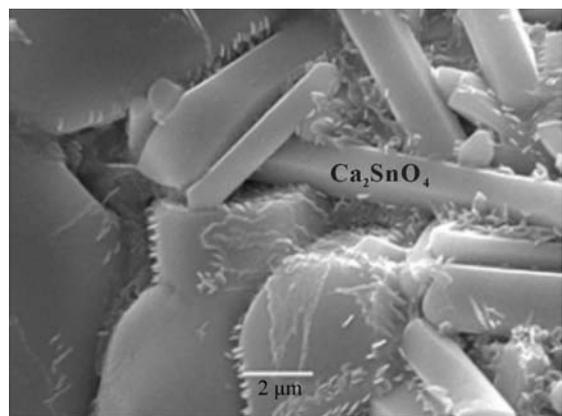
SnO <sub>2</sub> content (in wt%)	1 day	2 days	7 days	28 days
0.0	9.23	10.53	13.58	16.31
0.5	8.24	10.26	12.50	16.26
1.0	8.87	10.25	13.04	17.04
1.5	8.23	9.89	12.70	15.92
2.0	8.10	9.50	12.21	16.00

increases the melt production compared with the cassiterite-free one. Microanalysis shows incorporating Sn in the phase of C<sub>3</sub>S and not in C<sub>2</sub>S. Finally, needle-like crystals occur in the form of Ca<sub>2</sub>SnO<sub>4</sub> (Figure 10). In Figure 11 we present the EDX spectrum of needle-like crystals marking the Ca<sub>2</sub>SnO<sub>4</sub> formation in contact with C<sub>3</sub>S.

Our experimental results are follow those carried out by [7]. Further investigation suggests that cassiterite increase over 1 wt% could not improve the burnability behavior because of Ca<sub>2</sub>SnO<sub>4</sub> formation instead of alite and belite.

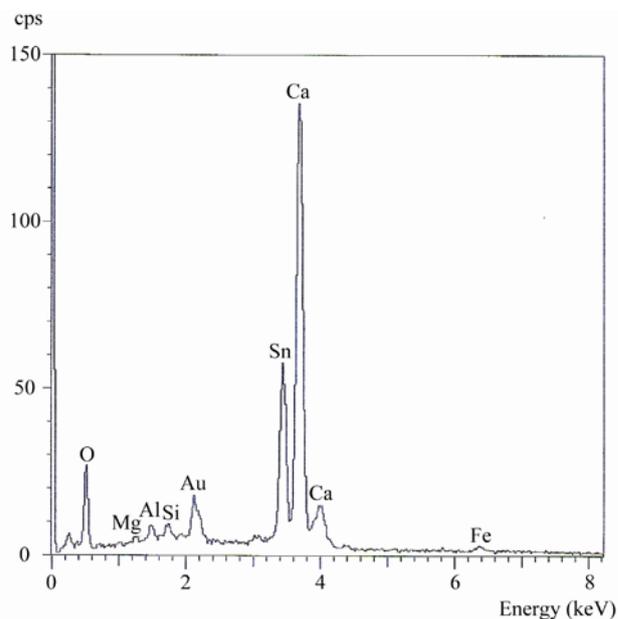


(a)



(b)

**Figure 10. (a) Formation of needle-like crystals of Ca<sub>2</sub>SnO<sub>4</sub> in contact with C<sub>3</sub>S. (b) Zoomed part of (a).**



**Figure 11. EDX spectrum of Ca<sub>2</sub>SnO<sub>4</sub> of needle-like crystals in contact with C<sub>3</sub>S (see Figure 10).**

#### 4. Conclusions

Our results show that during cement production adding cassiterite in the raw mix influences positively the heat treatment and lowers more intensively the values of free lime. Though we get the best results with SnO<sub>2</sub> = 1 wt%.

Therefore, the presence of cassiterite, results in the following: 1) promotes creating white, needle-like, crystals of Ca<sub>2</sub>SnO<sub>4</sub> and 2) easier formation of C<sub>3</sub>S (alite) instead of C<sub>2</sub>S (belite). Therefore Sn has the ability to incorporate into the crystal lattice of alite and cannot dissipate during cooling. Finally, cements that contain cassiterite as an admixture show a small delay in their early hydration at 1, 2 and 7 days, which stops after 28 days.

#### 5. Acknowledgements

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